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Date Out EFB:

0 2 FEB 1984

To:

Jay Ellenberger Product Manager 12 Registration Division (TS-767)

From:

Samuel M. Creeger, Chief Review Section No. 1

Exposure Assessment Branch Hazard Evaluation Division (TS-769)

Attached please find the environmental	fate review of:	
Reg./File No.: 464-448		
Chemical: Chlopyrifos		
Type Product: Insecticide		
Product Name: LORSBAN		
Company Name: Dow		
Submission Purpose: Review data submitt	ted to satisfy soil pho	otolysis
requirement		
ZBB Code: other	ACTION CODE: 336	
Date In: 11/2/83	EAB # 4082	
Date Completed:	TAIS (level II)	Days
	63	1
Deferrals To:	•	
Ecological Effects Branch		
Residue Chemistry Branch		
Toxicology Branch	· · · · · · · · · · · · · · · · · · ·	

1. INTRODUCTION

1.1 Dow Chemical has submitted photolysis data to satisfy the soil photolysis data gap.

2. DISCUSSION OF DATA

2.1 Chlorpyrifos Soil Studies, Experiment 78-2.

This study involved UV (254 nm) irradiation of the treated soil surface. Light of this wavelength is not representative of sunlight reaching the earth's surface. Therefore, this study alone will not satisfy the data requirement and is not reviewed in depth here. However, after 8 days of exposure, the study reports 60% parent remaining with only minor amounts of one product, which is probably 3,5,6-trichloro-2-pyridinol, loss of 10% of the applied activity due to volatilization and about 30% bound residues.

2.2 Chlorpyrifos Soil Studies, Experiment 79-6.

As stated in the report, details of methodology are not given but are available in the literature (citations not given). Therefore, this study cannot be reviewed at this time. However, since the study involves exposure of chlopyrifos-treated soil surfaces, it is possible that this study with all its details would satisfy the soil photolysis data requirement. This cannot be determined with certainty until the data are submitted for review.

2.3 Dissipation of Chlorpyrifos from Dry Soil Surfaces, Getzin, L.W. J. Econ. Entomol. 1981, 74, 707-713.

This study does not contain photolysis data.

3. CONCLUSIONS/RECOMMENDATIONS

3.1 The soil photolysis data requirement is not satisfied by the data in this submission. However, note the comment in section 2.2. above.

Samuel M. Creege February 2, 1984 Section #1/EAB

Hazard Evaluation Division

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Shaughnessey No. 059101

Date Out EFB: 1 5 NOV 1984

To:

J. Ellenberger

Product Manager 12

Registration Division (TS-767)

From:

Samuel Creeger, Chief Review Section No. 1

Exposure Assessment Branch

Hazard Evaluation Division (TS-769)

Attached please find the environment	al fate review of:	
Reg./File No: 44-448, -523 and -55	52	
Chemical: Chlorpyrifos		
Type Product: Insecticide		
Product Name: LORSBAN 4E, 15G and 50)W	
Company Name: Dow		
Submission Purpose: Review soil pho	otolysis study in suppo	rt of previous
request for use on various crops		
ZBB Code:	ACTION CODE:	305
Date in: 9/7/84	EFB #	4564-66
Date completed: 11/14/84	Tais (level I	I) Days
	62	2.0
Deferrals To:		
Ecological Effects Branch		
Residue Chemistry Branch		
Toxicology Branch		

1.0 INTRODUCTION

Dow Chemical Company is requesting ammended registrations for the use of chlorpyrifos (O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothicate) on tobacco, tomatoes, sorghum, citrus fruits (tank mix with Spray Oils), corn, cherries, figs, cranberries, alfalfa, grapes, soybeans, onions and peanuts. These amendments had been previously rejected by EAB because of a soil photolysis data gap for chlorpyrifos. The subsequently submitted soil photolysis data were found to be deficient (EAB review of 2/2/84). A new soil photolysis study has been submitted with this request.

2.0 DISCUSSION OF DATA

2.1 Photodegradation of Chlorpyrifos on Commerce Soil Surface. Yackovich, P.R. and Miller, J.H. Agrichemical Products Department, Dow Chemical. July 27, 1984. Acc. No. 254395.

Procedure:

Commerce soil (36% sand, 50% silt, 14% clay, 0.6% CC), a loam soil, was slurried with distilled water, plated onto 9 cm round glass plates and amended with ^{14}C -chlorpyrifos. The plates were placed in a water jacketed glass chamber, covered with a glass plate and irradiated with light from a mercury arc lamp. (See Figures 1 and 4 on page 4.). The source air passed over Drierite to remove moisture and a bed of Ascarite TM to remove CO₂ before passing over the soil coated glass plates. Volatiles were trapped in a polyurethane foam plug and $^{14}\text{CO}_2$ was trapped in a bubbler trap containing Carbosorb. (See figure 3 on page 5.)

Replicate treated and dark samples were taken at days 1, 3, 6, and 12 days for liquid scintillation counting (TLC), extraction, and combustion analysis. The extracts were analyzed by High Performance Liquid Chromatography (HPLC).

Results:

The recovery of ¹⁴C activity from the Commerce loam soil samples is summarized in Table 1 on page 6. Figures 5-8 on pages 7-10 give the amount of chlorpyrifos and its degradates found by HPLC in both treated and dark samples. Figures 9 and 10 on pages 11 and 12 graphically show the soil degradation of the parent and appearance of the photoproducts.

According to the registrant, chlorpyrifos did not follow first order kinetics. Instead, the data fit a non-linear regression analysis utilizing a two component model. This is shown in Figure 11 on page 13. The model assumes that the chemical resides in two soil compartments, one in which the chemical is available for degradation and another in which it is not. The kinetics are dependent on the degradation rate of the chemical in the available compartment and the transfer rate of the chemical between compartments. The plots of the computer generated analyses using the two compartment model is shown in Figures 12 and 13 on pages 14 and 15.

Conclusions:

Chlorpyrifos is rapidly degraded on soil both with light irradiation and without it. The degradation in both cases, however, is not linear. rapid degradation begins to slow around day 3. About 40% of the parent is degraded by 2.2 days with light and 3.2 days without light. The major degradate is 3,5,6-trichloro-2-pyridinol in both light and dark. In the light, however, a minor degradation product, 2-methoxy-3,5,6-trichloropyridine, is also formed.

The initial

While this study indicates that under the test conditions light has little effect on the degradation of chlorpyrifos, it is not conclusive that the same effect would be evidenced in natural sunlight. The mercury arc lamp used does not emit all of the wavelengths which are present in natural sunlight. Further, a glass plate of unknown transmissibility was used to cover the reaction chamber containing the soil plates. Some of the wavelengths which were emitted could have been absorbed by the glass. The submission of the UV absorption spectrum of chlorpyrifos would help the reviewer evaluate whether the wavelengths absent from the artifical source but present in natural sunlight, would be absorbed by the pesticide and thus be possible cause of further photodegradation. The report does not state how the intensity of light of the artificial source relates to that of natural sunlight.

Several other concerns are also noted. The non-linear nature of the degradation of chlorpyrifos on soil is explained as a two compartment model with one compartment being available for degradation and one being unavailable for degradation. The only support for this assertion is that the model fits the data. No explanation as to the nature of the unavailability of chlorpyrifos is given. Does this represent binding to the soil, a conformational change, or what? Also, while the first half-life of chlorpyrifos is 3-5 days, what is the second half-life? How resistant or susceptible to photolysis is chlorpyrifos after the initial rapid degradation?

3.0 CONCLUSIONS

- 3.1 Under the test conditions chlorpyrifos degrades non-linearly with little difference in degradation between irradiated and unirradiated soil.
- 3.2 The major photoproduct is 3,5,6-trichloro-2-pyridinol with a minor photoproduct being 2-methoxy-3,5,6-trichloropyridine.
- 3.3 The relationship of the artificial light source to that of natural sunlight was not given. The kind of glass and the transmissibility of the glass covering the reaction chamber was not given.

- 3.4 This study does not satisfy the photolysis data requirement for chlorpyrifos.
- 3.5 We need to know if the "compartmentalized behavior is unique to the single soil studied. Therefore, photolysis of chlorpyrifos on other soils should be studied.

4.0 RECOMMENDATION

In order for the reviewer to completely evaluate this study the registrant should submit information on the transmissibility of the glass plate used to cover the reaction chamber, the relationship of the artificial light intensity to that of natural sunlight, and the UV absorption of chlorpyrifos.

Further, to give some indication as to the nature of the non-linear degradation of chlorpyrifos, photolysis studies should be conducted on other soils. These studies should extend for the full 30 days to give a better indication of the photopersistance of chlorpyrifos after the initial rapid degradation. Soils from different but major chlorpyrifos use areas should be selected.

Norma Kay Whetzel November 14, 1984 Review Section No. 1 Exposure Assessment Branch Hazard Evaluation Division

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